traction into sodium chloride solution, and in the third potassium chloride penetrating by intertraction into potassium nitrate.

In the diagram are set out a series of results applying to magnesium sulphate superposed on cobalt chloride. It is divided into sections; in the first section (1–4) is depicted the progress of the intertraction, the analysis having been made after three different time-intervals. The lower sections (5 and 6) of the diagram are to be read in relation to No. 3.

In conclusion, I have much pleasure in expressing my thanks to the Committee of the Inoculation Department for the facilities afforded to me for the carrying out of this research, and to Sir Almroth Wright for the interest he has taken in this research and his kind assistance in framing this paper.

The Absorption Spectrum of Potassium Vapour.

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[Plate 5.]

1. *Introductory.*

In connection with the investigation of the vacuum arc spectrum of potassium,* which was undertaken mainly to improve the existing measures, it was found that the type of lamp used in that experiment was unsuitable for the production of the higher members of the series. Already Wood† has shown that the principal series of sodium is much more complete in the absorption than in the emission spectrum, and has extended the series up to $m = 57$. Bevan‡ repeated the experiments with the other alkali elements and was able to extend the principal series in each case very considerably. In view of the importance of obtaining accurate measures of these lines and a possible extension of the series, so that they may afford data which will help to throw some light on the question as to the nature of the formula giving series lines, it was thought desirable to repeat the experiment of Bevan with instruments of greater dispersion. The results which have been accomplished in the repetition of the work may be briefly summarised as follows:—

(1) The number of members of the series has been raised from twenty-four

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* 'Roy. Soc. Proc.,' A, vol. 99, p. 69 (1921).

† R. W. Wood, 'Astrophys. Journ.,' vol. 29, p. 97 (1909); R. W. Wood and R. Fortrat, 'Astrophys. Journ.,' vol. 43, p. 73 (1916).

‡ 'Phil. Mag.,' vol. 19, p. 195 (1910).

to forty-two. (2) The first seven members of the series have now been resolved into their components as compared with five in previous investigations. (3) Besides the absorption of the lines of the principal series, new lines have been found to be absorbed at somewhat higher pressure which seem to have no correspondence with the known lines in the emission spectrum. (4) An important result of the experiments is the observation of the absorption of the two combination lines 1*s*—2*d* and 1*s*—3*d*, the first as a pair confirming the presence of a satellite to the lines of the diffuse series, and the second as an unresolved line.

2. *Experiments.*

The metallic potassium was vapourised in a tube of steel, about 20 inches in length and 1 inch in diameter, heated electrically, so as to obtain proper control over temperature. The ends of the tube were closed with thin quartz lenses, attached with sealing-wax and kept cool by circulation of cold water through two jackets fitted on the ends of the tube. Previous to heating, the tube was exhausted by a Gaede pump, and during the experiment the vapour pressure of potassium was maintained nearly constant by a make-and-break arrangement in the heating circuit, which secured the necessary control. As the source of light, the white-hot crater of an ordinary carbon arc, maintained at 110 volts and about 12 ampères, was used. Besides giving out a strong continuous spectrum it emitted a few iron and other lines, which were used as comparison lines with advantage and provided the surest check against any mechanical shift. The temperature of the tube and the resulting vapour density of potassium were regulated according to the portion of the series under investigation. Preliminary experiments with a small quartz instrument revealed the fact that for the first few members the pressure should not exceed 8 mm. in order to obtain lines sharp enough for good measures. At this low density, however, members higher than 15 were not absorbed. Keeping the temperature low by intermittent exhaustion and raising the temperature of the tube by continuous heating, it was possible to extend the series up to $m = 26$, while maintaining the lines sharp. Absorptions of still higher members as fine lines were secured at a pressure of about 37 mm. at the sacrifice of the sharpness of the lines constituting the earlier members. At this stage the new lines also appeared.

Measurements were made on photographs taken in the second order spectrum of the 10-foot concave grating, giving a dispersion of about 2·8 Å.U. per millimetre. The wave-lengths of the reference iron lines were taken from the table given by Burns.

The new measures are collected in Table I:—

Table I.—Principal Series of Potassium. 1*s*—*mp*, 1*s*=35008·48.

λ I.A.	ν (vac.).	Δν.	$mp_{1,2}$.	*m*.	$\nu_{obs.}-\nu_{cal.}$
*7664·94	13042·82	57·71	21965·66	(1)	0·00
99·01	12985·11		22023·37		
†4044·140	24720·18	18·69	10288·30	(2)	0·00
47·201	701·49		306·99		
†3446·722	29004·70	8·15	6003·78	(3)	−2·53
47·701	8996·55		11·93		
3217·176	31074·22	4·43	3934·26	(4)	0·07
16·633	069·79		38·69		
3101·806	32229·96	2·25	2778·52	(5)	0·09
02·023	227·71		80·77		
3034·780	32941·76	1·65	2066·72	(6)	0·19
34·932	40·11		68·37		
2992·140	33411·18	1·11	1597·30	(7)	0·28
92·240	10·07		98·41		
2963·260	33736·78		1271·70	(8)	0·08
2942·718	33972·28		1036·20	(9)	0·17
2927·602	34147·68		860·80	(10)	0·04
2916·114	34282·20		726·28	(11)	0·11
2907·203	34387·28		621·20	(12)	−0·05
2900·126	34471·18		537·30	(13)	−0·06
2894·407	34539·29		469·19	(14)	0·06
2889·738	34595·09		413·39	(15)	0·01
2885·857	34641·62		366·86	(16)	0·10
2882·614	34680·60		327·88	(17)	0·06
2879·864	34713·70		294·78	(18)	0·04

λ I.A.	ν (vac.).	*mp*.	*m*.	$\nu_{obs.}-\nu_{cal.}$
2877·509	34742·11	266·37	(19)	0·08
2875·494	34766·46	242·02	(20)	−0·01
2873·743	34787·64	220·84	(21)	−0·04
2872·214	34806·15	202·33	(22)	−0·06
2870·865	34822·51	185·97	(23)	−0·03
2869·668	34837·05	171·43	(24)	0·09
2868·627	34849·80	158·68	(25)	0·03
2867·676	34861·24	147·24	(26)	0·06
2866·832	34871·50	136·98	(27)	0·10
2866·075	34880·72	127·76	(28)	0·11
2865·407	34888·84	119·64	(29)	−0·05
2864·778	34896·52	111·96	(30)	0·09
2864·213	34903·38	105·10	(31)	0·11
2863·703	34909·60	98·88	(32)	0·10
2863·244	34915·18	93·30	(33)	0·00
2862·823	34920·33	88·15	(34)	−0·06
2862·421	34925·23	83·25	(35)	0·04
2862·069	34929·54	78·94	(36)	−0·05
2861·71	34933·89	74·59	(37)	0·05
2861·38	34937·92	70·56	(38)	0·50
2861·07	34941·73	66·75	(39)	0·53
2860·83	34944·64	63·84	(40)	0·51
2860·51	34988·66	59·82	(41)	1·48
2860·32	34951·10	57·38	(42)	1·15

* Measures taken from Meggers.

† Vacuum arc measurements.

3. *Regularity of the Series.*

It is well known that the frequencies of any of the recognised series can be approximately given by a formula of the type $\nu = \mathrm{A} - \mathrm{N}/[f(m)]^2$. A convenient form of $f(m)$ is that suggested by Hicks, viz., $f(m) = m + \alpha + \beta/m$. Assuming N to be known, the limit A of the series, as well as its other constants, are usually calculated from the lines giving the earlier members of the series. The actual calculated value of A then not only suffers from the errors of observation of the three lines, but also depends to a considerable extent on the form of $f(m)$ employed and the value of the constants α, β. It is evident that in the case where many members of a series are known, the limit might be best obtained from the higher members. And although it may be objected that these higher members, being in the ultra-violet small observational errors in wave-lengths, are multiplied by large factors in the wave numbers, by taking a sufficient number of them into account the mean will give a more trustworthy result than is obtainable by any other means. Prof. Nicholson* has suggested a method for the accurate determination of the limit of the series which involves the above mode of treatment. The method requires for its application a preliminary formula, for example, of the Hicks type, for the expression of the series. If the series is represented by

$$\nu_m = \mathrm{A} - \mathrm{N}/(m+\alpha+\delta)^2,$$

then

$$\nu_m = \mathrm{A} - \frac{\mathrm{N}}{(m+\alpha)^2}\left[1 - \frac{2\delta}{m+\alpha} + \frac{3\delta^2}{(m+\alpha)^2} - \dots\right].$$

The fourth term of the convergent series is $3\mathrm{N}\delta^2/(m+\alpha)^4$, and since N is about 10^5, this cannot exceed a certain value which will affect the significant figure in A beyond a certain value of m depending on the value of δ used. For all the lines beyond that value of m,

$$\nu_m = \mathrm{A} - \frac{\mathrm{N}}{(m+\alpha)^2} + \frac{2\mathrm{N}\delta}{(m+\alpha)^3},$$

whence,

$$\mathrm{A} = \frac{(m+1+\alpha)^3\,\nu_{m+1} - (m+\alpha)^3\,\nu_m + \mathrm{N}}{(m+1+\alpha)^3 - (m+\alpha)^3}.$$

If N is known, this formula would permit a determination of the limit of the series from any pair of consecutive lines. Taking $\mathrm{N} = 109678{\cdot}31 + \Delta\mathrm{N}$, where $\Delta\mathrm{N}$ represents the difference of N for potassium from that for hydrogen determined accurately by W. E. Curtis,† A can be calculated and will include a known and an unknown part involving $\Delta\mathrm{N}$. The formula adopted by Prof. Fowler‡ for the principal series of potassium is

$$\nu\,(m) = 35005{\cdot}88 - \mathrm{N}/(m + 1{\cdot}296281 - 0{\cdot}061661/m)^2.$$

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* J. W. Nicholson, 'Roy. Soc. Proc.,' A, vol. 91, p. 255 (1915).

† W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 90, p. 605 (1914).

‡ A. Fowler, 'Report on Series in Line Spectra,' p. 101.

Taking these values of the constants, it can be shown that for lines beyond $m = 9$, the fourth term mentioned above is negligible.

Considering some of the lines beyond $m = 9$, the values of A have been calculated by Nicholson's method, giving the results shown in Table II.

Table II.

Calculated from lines $m =$	A.	
10, 11	35008·38	$+\Delta N/418$
13, 14	35008·48	$+\Delta N/657$
14, 15	35008·08	$+\Delta N/749$
19, 20	35008·15	$+\Delta N/1297$
24, 25	35009·27	$+\Delta N/1996$
25, 26	35008·89	$+\Delta N/2154$
26, 27	35009·99	$+\Delta N/2318$
28, 29	35006·79	$+\Delta N/2663$
31, 32	35007·88	$+\Delta N/3226$
33, 34	35007·78	$+\Delta N/3632$

No value of ΔN can be found which makes the general deviations from equality any smaller than they are for the calculated parts at present. This does not necessarily mean that $\Delta N = 0$, but that the method is not suitable for the calculation of ΔN with the available observations. But as any reasonable value of ΔN will only affect the second decimal figure in the value of A, ΔN may be assumed to be zero. The mean value of A thus obtained is $A = 35008{\cdot}48$.

With this limit and any two other lines it is possible to calculate the series, but it is found that unless the earlier members are used for the calculation of constants, the difference in the observed and the calculated wave numbers far exceeds the limits of observational error, perhaps due to the important part which ΔN plays for these earlier members. A formula which represents the whole series very closely has been obtained with the above limit and the stronger components of the first and second lines, namely,

$$p_1(m) = 35008{\cdot}480 - 109736{\cdot}1 \Big/ \left(m + 1{\cdot}29667 - \frac{0{\cdot}06154}{m}\right)^2.$$

With the value of $N (= 109736{\cdot}1)$ obtained by taking the mass correction of the nucleus of potassium into account, the agreement between the observed and the calculated values (shown in Table I) is somewhat better than when the value of N for hydrogen (109678·3) is used. Except for the deviation shown at $m = 3$, which is rather abnormal, and the last four members ($m = 39$ to 42), the agreement is within the errors of observation, which are believed to be not greater than 0·01 A. The deviations of the higher members ($m = 39$ to 42) are supposed to be real, as the change in the value of N due to any perturbation, or those of the constants α and β, have very little effect for higher values of m. It may be mentioned here that the principal series of sodium also shows similar deviations for the last few lines, and Prof. Hicks* has expressed his doubts whether they actually belong to the typical p series. It is, however, possible to extend an idea of Prof. Sommerfeld to these higher members which may explain the observed deviation. Prof. Sommerfeld, with a view to explaining the continuous spectrum which usually appears† at the end of the series, has put forward the theory that, when the radiating electron is knocked out of the atom, it comes into collision with other free electrons or atoms, and consequently, when it falls back to the limiting orbit and forms part of the atom, the extra energy received during the collision has also to be taken into account.

As the electron can acquire any velocity during such collision, the extra energy ($\frac{1}{2}\mu v^2$), where μ is the mass of the electron and v the velocity acquired, may have any value from zero upward. Consequently the electron, in falling to the limiting orbit, would not give rise to a line (the limit of the principal series), as is to be expected from Bohr's theory, but a continuous spectrum stretching on the more refrangible side of the limiting line. Now the condition of the electron, owing to the very weak influence of the nucleus in any of the very high orbits (almost approaching the limit), is not very different from one entirely removed from the atom. So that it possibly acquires extra energy in a similar way. And if the energy received be not sufficient to ionise the atom or to raise the electron to higher orbits, then there will be an increase in the amount of energy radiated. The total effect of this would be to broaden the lines (as they are known to be), with the consequent displacement of the line on the more refrangible side. In both sodium and potassium, the observed frequency is higher than the calculated one for the last few lines.

4. *Absorption of Lines other than the Principal Series.*

Besides the absorption lines of the p series, several new lines were absorbed at higher pressure, of which no traces could be found at low pressure. The experiments on absorption were carried on at five different pressures: 2·5 mm., 5 mm., 20 mm., 37 mm., and 46 mm. These new lines made their first appearance at 20 mm. pressure, strengthening in intensity, and becoming diffuse as higher pressures were reached. Up to $m = 6$, lines were observed on both sides of the p series lines. At $m = 2$, the lines are far removed from the p series line, but they gradually approach and finally coalesce with the p series lines with decreasing intensity as $m = 7$

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* W. M. Hicks, 'Astrophys. Journ.,' vol. 44, p. 229 (1916).

† It is most striking in the case of the Balmer series of hydrogen, especially as it appears in some of the stars.

is reached. At $m = 6$ another set of lines appear, which run parallel with the p series lines in the scale of oscillation frequency and on their more refrangible side.

These lines seem to have no correspondence with the emission lines of potassium, and attempts to correlate them have not been successful. Their wave-lengths and wave numbers corrected to *vacuo* are collected in Table II. The wave-lengths of the nearest p series lines are also given, in order to show their divergences from them.

Table III.

Converging Set.				Parallel Set.			
Designation.	λ I.A.	ν (vac.).	$\Delta\nu$.	Designation.	λ I.A.	ν (vac.).	$\Delta\nu$.
New	Merged into the broad violet band.						
p_2 (2)	4047 ·201			p_1 (6)	3034 ·780	32941 ·76	19 ·33
p_1 (2)	4044 ·140	24720 ·18	113 ·86	New	3033 ·0	961 ·09	
New	4025 ·6	24834 ·04		p_1 (7)	2992 ·140	33411 ·18	18 ·88
New	3461 ·7	28879 ·2	117 ·4	New	2990 ·45	430 ·06	
p_2 (3)	3447 ·701	28996 ·55		p_1 (8)	2963 ·260	33736 ·78	17 ·69
p_1 (3)	3446 ·722	29004 ·70	101 ·6	New	2961 ·71	745 ·47	
New	3434 ·7	29106 ·3		p (9)	2942 ·718	33972 ·28	17 ·62
New	3221 ·8	31029 ·9	46 ·9	New	2941 ·19	989 ·90	
p_2 (4)	3217 ·663	31069 ·79		p (10)	2927 ·602	34147 ·68	17 ·57
p_1 (4)	3217 ·176	31074 ·22	32 ·9	New	2926 ·10	165 ·25	
New	3213 ·8	31107 ·1		p (11)	2916 ·114	34280 ·20	18 ·88
New	3103 ·4	32213 ·4	14 ·3	New	2914 ·51	01 ·08	
p_2 (5)	3102 ·023	32227 ·71					
p_1 (5)	3101 ·806	32229 ·96	13 ·5				
New	3100 ·5	32243 ·5					
$p_{2,1}$ (6)	New lines are too feeble to measure.						

5. *Absorption of the Combination Lines* 1*s*—2*d*, 2*d′ and* 1*s*—3*d*.

One of the most interesting results achieved in the repetition of the experiment is the absorption of the two combination lines 1*s*—2*d* and 1*s*—3*d*. Previous to this only the lines of the principal series have been observed in absorption. According to Bohr's theory the radiating electron is in the 1*s* orbit in the quiescent state of the atom, and the absorption of energy causes its transfer from the 1*s* orbit to the successive orbits. The absorption of practically all the members of the principal series clearly suggests that the energy absorbed in the process is very nearly that required to ionise the atom if not actually ionising it. In the scale of energy, the positions of the *d* orbits are much nearer to the 1*s* orbit than even the 2*p* orbit. Consequently it was considered very remarkable that the energy sufficient to knock out the electron from the atoms was not sufficient to transfer it to the *d* orbits.

According to Sommerfeld these lines represent an interorbital transition requiring a change of two units in azimuthal quantum, which is forbidden according to the selection principle of Bohr or Rubinowicz. While the line is well known, its excitation has been thought to be occasioned by the presence of the electrostatic field. In the present case, however, it is difficult to conceive of any external electrostatic field. The possibility of the influence of the electric field due to the neighbouring atoms is also precluded from the fact that these lines were observed at even the lowest pressure (2·5 mm.). Had there been any such field of atomic origin their effect on the bands of potassium, which were simultaneously absorbed, would have been too great to escape notice. Absorption bands of potassium, though faint, were beautifully sharp at 2·5 mm. pressure, and no blurring was noticed till the pressure reached as high as 30 mm., when the flutings merged into a continuous mass owing to the acknowledged Stark effect. The intensity of the combination lines, however, increased with an increase in pressure; but this may mean more than anything else that, at low pressure, owing to the smallness of the number of absorbing atoms, the chances of such extraordinary transfers are very rare. The effect of increase of pressure is to increase the chances by increasing the number of atoms. The possibility of bringing out these transfers, without an external field is proved beyond doubt by the beautiful experiments of Foote and others,* who observed the radiation of the combination lines $1s$—$2d$, $2d'$ in the space shielded from the applied electrostatic field—itself very low.

This result and that of Foote and others may, therefore, be pointed to as distinct evidence of contradiction of the selection principle as at present enunciated.

The combination lines $1s$—$2d$ were observed as a pair, as previously recorded,† and may be put forward as an indication of regarding the diffuse lines as having a satellite.

The line at about λ3650 was photographed with a small quartz spectrograph in the vacuum arc experiment and was recognised as the combination $1s$—$3d$.‡ This was, however, not included in the previous paper owing to the rough nature of its measure. This was observed as an absorption line in the present experiment, its wave-length having the value—

$$\lambda\ 3648{\cdot}971, \qquad \nu\,(\text{vac.})\ 27397{\cdot}19, \qquad \nu_{\text{cal.}}\ 27397{\cdot}6.$$

The absorption of all the lines, one of whose terms is $1s$, gives an additional

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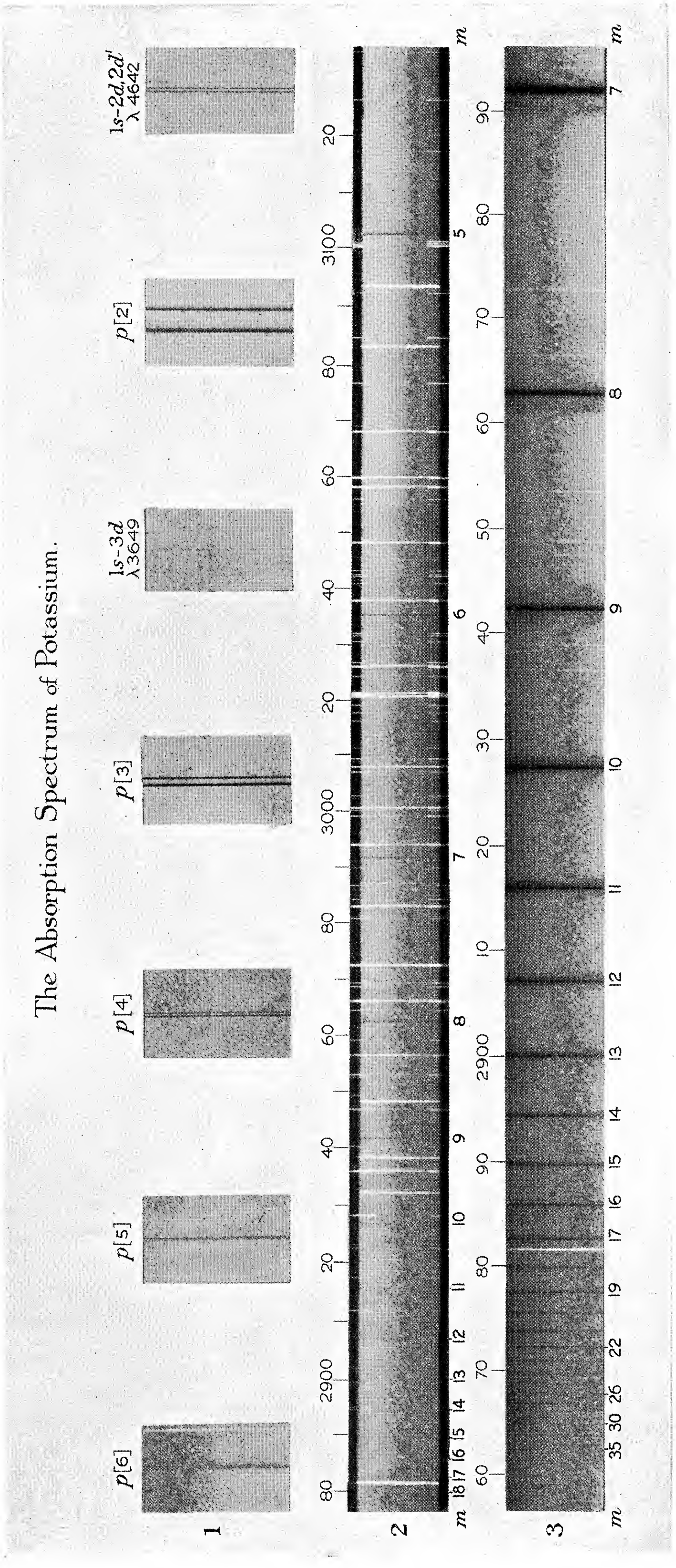
* P. D. Foote, W. F. Meggers, and F. L. Mohler, 'Astrophys. Journ.,' vol. 55, p. 145 (1922).

† 'Roy. Soc. Proc.,' A, vol. 99, p. 69 (1921).

‡ See A. Fowler, 'Reports on Series in Line Spectra,' p. 103.



The Absorption Spectrum of Potassium.

stress to the 1*s* orbit as being the significant one. The significance of 1*s* orbit according to Bohr's theory is that it represents the orbit of the electron in the normal state of the atom. Consequently the chances for all radiations one of whose terms is 1*s* are very great. Increasing, therefore, the chances alone by appropriate experiments, the absorption of lines corresponding to other interorbital transfers may possibly be obtained.

The absorption *bands* of potassium have also been photographed and will form the subject of a separate communication.

Summary.

1. The principal series lines up to $m = 42$ have been observed as absorption lines and their wave-lengths accurately measured. The series equation shows satisfactory agreement between the observed and the calculated values with the exception of deviations for the last few lines for which a possible explanation has been given.
2. The first seven members of the series have been resolved into their components as compared with five in previous investigations.
3. Besides the absorption of the lines of the principal series, new lines have been found to be absorbed at higher pressures, which seem to have no correspondence with the known lines in the emission spectrum.
4. The combination lines 1*s*—2*d* and 1*s*—3*d* have been found to be absorbed, the first as a pair, confirming the presence of a satellite to the lines of the diffuse series. Their appearance in the absorption spectrum gives distinct evidence of contradiction of the selection principle.

In closing, my best thanks are recorded to Prof. A. Fowler, F.R.S., for his helpful interest in the work.

DESCRIPTION OF THE PLATE.

Fig. 1.—Showing the combination lines 1*s*—1*d*, 2*d*′ ; 1*s*—3*d*, and the earlier members of the principal series in order of decreasing wave-length. *p* [6] is from an enlargement of a second order negative, all others are from that of a first order.

Fig. 2.—Showing the absorption of the principal series lines from $m = 5$ to 18, at a pressure of 5 mm.

Fig. 3.—Showing the absorption of the principal series lines from $m = 7$ to 42, at a pressure of 46 mm.

The Absorption Spectrum of Potassium.

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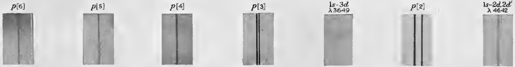

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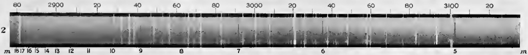

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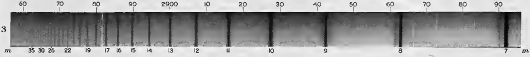

DESCRIPTION OF THE PLATE.

Fig. 1.—Showing the combination lines $1s-1d, 2d'$; $1s-3d$, and the earlier members of the principal series in order of decreasing wave-length. $p[6]$ is from an enlargement of a second order negative, all others are from that of a first order.

Fig. 2.—Showing the absorption of the principal series lines from $m = 5$ to 18, at a pressure of 5 mm.

Fig. 3.—Showing the absorption of the principal series lines from $m = 7$ to 42, at a pressure of 46 mm.